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By JAMES EDGAR BELL
B.S. UNIVERSITY OF CHICAGO, 1905

THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS

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AN IMPROVED METHOD FOR DETERMINING THE EQUIVALENT CONDUCTANCES OF STRONG ELECTROLYTES AT INFINITE DILUTION.[1]

PART I.—THE NATURE OF THE PROBLEM.

Introduction.

Equivalent conductances of aqueous solutions of salts are seldom determined at higher dilutions than ten-thousandth normal. A few experiments[2] have been made with solutions more dilute but the experimental errors in such work are very large, and the values obtained are known to be unreliable. In fact, there is considerable doubt as to the accuracy of the values commonly accepted for ten-thousandth normal solutions. This uncertainty is due to the following three sources of error:

(1) In all conductivity experiments in highly dilute solutions, a large "water correction" is necessary. The exact magnitude of this correction and the proper method of applying it are very uncertain.

(2) If solutions are made up in contact with the air, this is always a fruitful source of contamination and one which has never been taken into account; if they are allowed to stand in glass vessels the glass becomes a probable source of pollution.

(3) The specific resistance of solutions of such low concentrations is very large and the difficulty in making accurate measurements is thereby greatly increased.

The Water Correction.

That the conductivity of the water itself is an important factor can readily be seen from a consideration of the measurements made by Kohlrausch and Maltby[3] on the alkali chlorides and nitrates. These experimenters made their solutions from water having a specific conductivity ranging from 0.9×10^{-6} to 1.06×10^{-6} reciprocal ohms. The accompanying table affords a comparison of the specific conductances of NaCl solutions at different concentrations, with the specific conductance of the water used in making the solutions. The values are for 18° C.

[1] Under the title of Part II, that part of the thesis was published in the *J. Am. Chem. Soc.*, **35**, 177–84 (1913).

[2] Whetham and Paine, *Proc. Roy. Soc.*, **81**, 58 (1908) have measured the conductivity of 0.00005 N H_2SO_4, and Kohlrausch and Maltby, *Abhandl. Physik. Tech. Reichanstalt*, **3**, 206 (1900) have made measurements on some alkali chlorides and nitrates at greater dilutions.

[3] Kohlrausch and Maltby, *loc. cit.*; also *Sitz. ber. Königl Preuss. Akad.*, **1899**, 665.

Conc. of NaCl.	Specific conductance times 10^6.
0.001 N	106.48 ohms
0.0001	10.81
0.00001	1.089
0.000001	0.109[1]
Water	1.03

The correction to be applied to the measured specific conductance is about 1% for 0.001 N; 9% for 0.0001 N; and 50% for 0.00001 N NaCl, while the determination of the conductance of millionth normal NaCl would be little better than a rough guess. By applying the correction, fairly accurate results might be obtained in solutions down to 0.0001 N or even 0.00001 N, were it not for the doubtful effect of added salts on the impurities, and consequently, on the initial conductance of the water. The uncertain factor in experiments of this kind can not be entirely eliminated but can be reduced by the use of purer water, *i. e.*, water of smaller specific conductivity. If water could be obtained whose initial specific conductance were negligible in comparison with that of the salt, as it is in higher concentrations, correct values would be obtained. It seems highly improbable, however, that solutions of this kind can ever be made for concentrations as low as 0.0001 N, since a sodium chloride solution of this strength made from the purest water ever obtained[2] and measured at 18° C., would have a water correction of nearly 0.4%. It might not be without interest to see what the water correction would be for solutions of NaCl and KCl of different concentrations and at different temperatures if this "perfectly pure" water of Kohlrausch and Heydweiller were used in their preparation. The following table gives the approximate corrections in percentage of total conductances of solutions of these two salts:

	Water correction.					
	NaCl.			KCl.		
Concentration of salt.	0°.	18°.	25°.	0°.	18°.	25°.
0.0001 N	0.2	0.4	0.46	0.17	0.3	0.38
0.00001 N	2.0	2.5	4.4	1.7	3.0	3.7
0.000001 N	17	27	31.4	15	33	28

No water that has been used in the preparation of salt solutions approaches the purity of the water referred to. That used by Kohlrausch and Maltby[3] had a conductivity twenty-five times as great.

Contamination of Solutions.

As to the contamination of solutions in the process of making or on standing for a while in glass vessels one has only to observe the increase in the

[1] In this case the calculated value at infinite dilution is used; the other values are from Kohlrausch and Maltby's data.

[2] Kohlrausch and Heydweiller, *Z. physik. Chem.*, **14**, 317 (1894).

[3] *Loc. cit.*

conductivity of fairly pure water when subjected to similar treatment. In transferring from one vessel to another, except with especial care, the conductivity may rise from 0.25 or 0.3 $\times$ 10^{-6} mhos to 0.4 or 0.6 $\times$ 10^{-6}. A similar increase in conductivity is found, if water is kept for a few minutes in the ordinary conductivity cell. Kohlrausch and Maltby[1] concluded that even though exact measurements of 0.00001 *N* solutions were made, the change in conductivity due to pollution of the water was relatively so high that one could no longer attach any significance to the results. In this region they did not always find the equivalent conductance to be greatest at the highest dilution, *e. g.*, at one, two and four, hundred-thousandth normal, the equivalent conductances of NaCl solutions were respectively, 108.86, 108.97 and 108.75. This problem, then, is certainly an important one and the more important does it become the greater the dilution, since the water correction increases with the dilution.

The Kohlrausch Method of Conductance Measurements.

Conductance measurements by means of the Wheatstone bridge with an induction coil as source of current and a telephone as balance indicator were described by F. Kohlrausch[2] over thirty years ago. The method was the outgrowth of polarization difficulties encountered in using a direct current and galvanometer. Use of the alternating current to avoid polarization had previously been made by Kohlrausch and Nippoldt[3] in 1869, and it is probable the telephone has been tried and discarded by others before Kohlrausch took it up in 1879 and made its application successful. Since that time the direct current and galvanometer have been but little used for electrolytic conductance measurements, their use being confined to exceedingly high resistances approaching a megohm in value.

Many refinements have since been made in the apparatus so that much more accurate results are obtainable now than originally. Most of the improvements were made by Kohlrausch himself who increased the length of the bridge wire thus making it more sensitive to slight changes in the unknown resistance, and did various things to improve the minimum. The latter problem led him into an investigation of the causes of poor minima,[4] such as polarization, self induction and capacity, as well as changes in conductivity due to heating effects of the electric current. In moderately dilute solutions he was able either to practically eliminate these disturbing elements or to counteract their influence by use of a condenser. But in very concentrated or very dilute solutions the difficulties did not altogether disappear.

The most disturbing of these factors in dilute solutions is capacity.

[1] *Loc. cit.*

[2] Wiedemann *Annalen*, **11**, 653 (1880).

[3] *Pogg. Annalen*, **138**, 280 (1869).

[4] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte."

Whenever resistances above a few hundred ohms are to be measured capacity troubles appear, and they increase as the resistances get larger. The so-called Chaperon[1] winding of resistance coils designed to eliminate capacity effects are much better than ordinary bifilar coils, but even these give difficulty and the last appeal is to Kohlrausch's method of using a condenser. This instrument is placed where it will do the most good and the capacity is varied until that value is found which gives the best minimum.[2] The best adjustment of the condenser is sometimes quite difficult to make and can be obtained only after much changing of plugs and considerable expenditure of time. Still it is one of the most important factors in getting correct bridge settings and is absolutely indispensable. In large resistances, a very small change in the capacity of the condenser

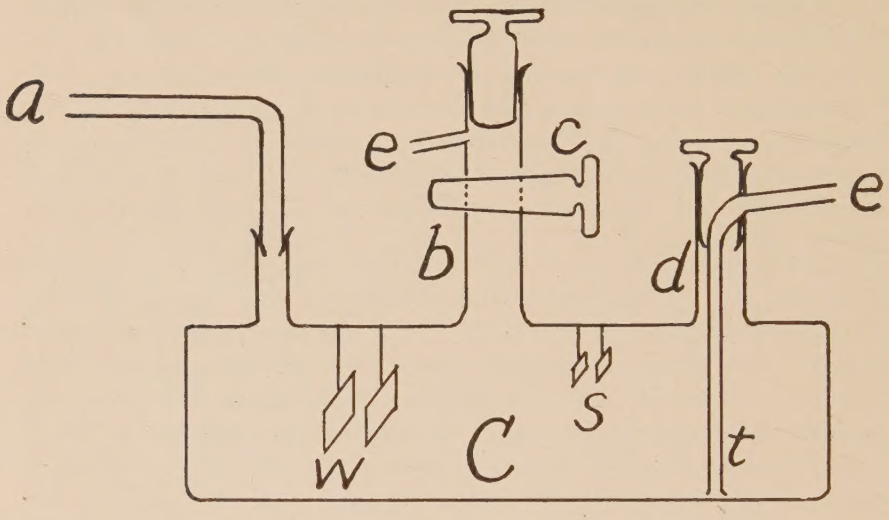

Fig. 1.

may alter the quality of the minimum considerably. I have noticed, in determining the conductivity of water, in which the temperature of the water had not yet acquired the temperature of the bath, and the bridge reading was, consequently slowly creeping, that the capacity with which a perfect minimum was obtained at one bridge reading was noticeably different from that with which a perfect minimum was obtained when the bridge reading had changed but a single space, the length of the bridge wire being 1000 spaces. This only shows how intimately related is a good minimum to the proper adjustment of the condenser and how important

[1] Chaperon, M. G., *C. R.*, **108**, 799 (1889).

[2] For this purpose Kohlrausch has devised a condenser containing units varying in value from 256, 128, 64, etc., down to $^1/_2$ so that is is possible to adjust the capacity to within $^1/_2$ of one of these units. A more convenient type is available and has been used in this work. It is referred to later.

the latter instrument is in this kind of work. It also explains why poor minima are probably the rule in conductivity experiments rather than almost perfect ones.

From the foregoing discussion of sources of error and survey of the method in common use we get a fair conception of the problem of conductance measurements. We are also enabled to see why work has not been extended into the region of still more dilute solutions and why more reliance cannot be placed upon some of the accepted values for the region that has been studied. It is clear that in any attempt to push the investigation into solutions of lower concentrations, the mode of attack must contain a scheme for decreasing the water correction. Furthermore, this scheme must arrange for getting purer water at the start and for preventing contamination in the process of solution making. These two factors are taken into account in the present work. The general plan is shown in Fig. 1 and consists in carrying out the entire procedure *in vacuo*, distilling the water directly into the cell C containing electrodes W for measuring its conductivity and electrodes W or S for measuring the conductivity of the solution. It likewise provides a means for introducing salts into the cell without danger of admitting air. This is done through the tube *b* and large stopcock *c*. The tube *a* comes directly from the still and makes an air-tight connection. At *d* is provided a means for either emptying the cell through the tube *t* or by turning *d* half around, simply exhausting without emptying. *e* leads to the pump.

In this way errors due to contamination in solution making will be practically eliminated and those due to the otherwise unavoidable water correction can, by careful work, be diminished to much smaller ones than is usually the case. In addition, improvements have been made in the Kohlrausch apparatus so that the electrolytic resistances may be determined with a much greater degree of accuracy than has hitherto been done.[1]

PART II.—AN IMPROVED APPARATUS FOR MEASURING THE CONDUCTIVITY OF ELECTROLYTES.

The problem demanded first of all a consideration of the Kohlrausch method in some of its details and its application to the measurement of electrical conductivities in aqueous solutions of strong electrolytes in the concentration range included between 0.001 and 0.000001 normal. As a result of a critical examination of the sources of error in this method when applied to solutions of such high specific resistances an apparatus has has been evolved which permits the *easy* attainment of a very high degree of precision, not only in the measurement of very large electrolytic resistances but of very small ones as well. In addition to the increased

[1] The apparatus devised for this purpose was found to be inadequate in some ways. It is being modified and the work continued by Mr. R. E. Baker.

degree of precision attained with the improved apparatus, it possesses the advantage of greater rapidity and convenience, and the sharp, perfect minima, obtained relieve the nerves of the operator of the strain imposed by the effort to find the correct bridge setting with a poor minimum. The apparatus described below was designed to include all of the perfections of the most accurate apparatus employed by Kohlrausch[1] together with some additional improvements which permit the attainment of a degree of precision, about ten times that obtained by Kohlrausch in his most accurate investigation. This high degree of precision is, moreover, attained with the greatest ease and certainty as will be clear from the test experiments described below A consideration of the theory of conductance measurements with the alternating current made it appear very probable that the precision of the method could be increased by making the following changes in the customary apparatus:

1. Abandon the induction coil as a source of current and replace it by a high frequency generator giving a pure current of a single frequency, one which is entirely free from the overtones which are present in the complex wave system obtained with the induction coil

2. For measuring very *high* resistances (20,000 ohms or more) replace the ordinary resistance box by one in which the resistance units are free from both inductance and capacity.

3. Use a tuned telephone, and an "extended" bridge wire and make all measurements at the middle of the bridge. Take as much pains in balancing the capacities in the bridge arms as in balancing the resistances.

Description of the Apparatus.

The High-Frequency Generator.—The only instrument on the market, as far as I was able to learn, which possessed most of the desired qualities was the "Small High-Frequency Machine" manufactured by Siemens and Halske. This machine has a normal frequency of 1000 cycles per second but any desired frequency between 450 and 1800 cycles per second can be obtained by regulating the position of the eddy-current "brake" provided with the instrument. This instrument is mounted upon a felt pad in a room some distance from the conductivity laboratory and is enclosed in a box to protect it from the dust and to shut in the sound emitted by the rapidly moving toothed wheel.

All of the connections for the instrument are brought to the main electrical distribution board of the building. The starting rheostat and the eddy-current brake are placed in the conductivity laboratory, the latter instrument being mounted near the conductivity bridge, so that the operator can vary the frequency of his current at pleasure. The

[1] As described in the paper of Kohlrausch and Maltby, *Abhandl. Physik. Tech. Reichsanstalt*, **3**, 157 (1900).

normal frequency of the instrument, 1000 cycles per second, is the best to employ in nearly all cases. Since, however, the frequency depends upon the rate at which the motor is driven, it is influenced by any sudden change in the load on the 110 volt circuit from which the motor is operated. Such changes, if they are not too frequent, can be readily neutralized by shifting the position of the eddy-current brake, but if they are liable to occur frequently they become a source of considerable annoyance. It is best, therefore, to operate the machine on a circuit of constant potential. In most of the experiments described below the machine was driven from a small 110 volt generator which was protected from a varying load. Under these conditions it has never been found necessary to vary the frequency.

The current obtained from the high-frequency generator is regulated by means of a rheostat mounted beside the starting rheostat of the generator, and connected in series with the exciting coil of the electro-magnet. The exciting current employed during the conductance measurements was varied according to the resistance of the cell, from 0.2 amp. for low resistances to 2.3 amp. for high resistances. The heating effect of the induced current in the cell, during the time required by the measurements, is scarcely appreciable with a properly designed cell, if an accuracy no greater than 0.01% is sufficient.

The Special "Film" Resistance Units.—In order to prepare stable high resistances, practically free from either inductance or capacity, it is only necessary to seal two platinum wires into the ends of a glass rod and connect them by a thin film of platinum deposited upon the glass. For the preparation of thin metallic films of this character a number of different methods have been devised and published in recent years.[1]

One of the most convenient methods makes use of a colloidal solution of the metal in a suitable solvent. One of these solutions, under the name of "platinum-glanz," is extensively employed in making gas electrodes.[2] The procedure employed in making resistance units with this material is as follows:

Two lead wires of platinum are sealed into the ends of a U-shaped glass rod of suitable length. The joint between the glass and the platinum is then covered with a layer of the platinum-glanz and by means of a drawing pen a narrow line of the platinum-glanz is drawn along the surface of the rod so as to connect the two lead wires. After the layer of platinum-glanz is completely dry it is heated gradually to a dull red heat. This heating

[1] L. Houllevigue, *Compt. rend.*, **149**, 1368; M. U. Schoop, *Electrochem. Z.*, **17**, 53; *Met. Chem. Eng.*, **8**, 404; H. G. Cannegieter, *Z. biol. Technik. Meth.*, **2**, 21; J. K. A. U., Salomonson, *Z. biol. Tech. Meth.*, **1**, 35–43; Leithäuser, *Engineering*, **86**, 818.

[2] In the later work a colloidal solution of chloroplatinic acid in oil of lavender was used.

can, with care, be conducted in a flame, but it is safer to use an electric furnace. When the heating is completed the narrow line of platinum-glanz has been converted into a thin film of platinum which is fused into the glass so that it cannot be scratched with a knife. A resistance unit of 80,000 ohms can be obtained in this way upon a U-shaped, narrow, glass rod only 10 inches high.

When properly constructed and handled these resistances are very permanent. They have a temperature coefficient of 0.1% per degree between 25° and 50°, and hence where an accuracy of 0.01% is desired the temperature of the resistance box must be kept constant to 0.1° during the measurement. The resistances of this type are mounted in regular resistance-box-form in an oil bath, provided with a thermometer, stirrer and heating coil. Since they are designed to serve as secondary standards only, they are checked at frequent intervals against a standard resistance box, using a galvanometer and direct current.

The Telephone.—Two telephones connected by a head piece constitute the most convenient arrangement. Both telephones should be tuned to respond to the frequency of the current employed. Those employed in the experiments described below were constructed especially for this work and were tuned to a frequency of 1000. Such an instrument is extremely sensitive when employed in a circuit of its own frequency.

The Bridge.—When a precision of more than 0.05% is desired in conductivity measurements it is necessary to lengthen the ordinary bridge wire. This is most conveniently accomplished by connecting to each end of the wire a resistance coil, having a resistance $4^1/_2$ times that of the bridge wire itself.[1] The bridge employed in the experiments described below was the Leeds and Northrup roller type, with two such coils mounted in the base so that by removing a couple of plugs the coils could be connected to the ends of the bridge wire. When these coils were so connected, the "extended" bridge wire thus obtained was equivalent to a wire 47 meters long. The smallest scale division was 3 mm. wide and corresponded to $^1/_{20,000}$ of the total length of the extended wire. Since the bridge setting could be *easily* read to less than 0.1 of a scale division, the error in a conductance measurement due to the error in *reading* the bridge setting could never amount to 0.2×0.0001 or 0.002%, for a setting at the middle of the bridge.

The Condenser.—The type of condenser devised by Kohlrausch[2] and used chiefly in this sort of work is not well adapted for getting the best minima. This is especially true in cases such as I have mentioned, where the condenser adjustments for two resistances quite close together, are noticeably different. A better instrument is one whose capacity may

[1] Kohlrausch and Holborn, p. 43.

[2] *Loc. cit.*

be varied continually from zero to the full capacity of the condenser. For the final adjustment, at any rate, an instrument of this kind should be available—one of the usual form being arranged in parallel with it if necessary.

By using a condenser of this type it is quite easy to find the best adjustment when the bridge setting is in the vicinity of the correct reading. In turning the button of the condenser to the right or left one passes through a point of minimum sound just as in adjusting the bridge reading. By alternately adjusting the two instruments the best minimum is quickly and easily obtained.

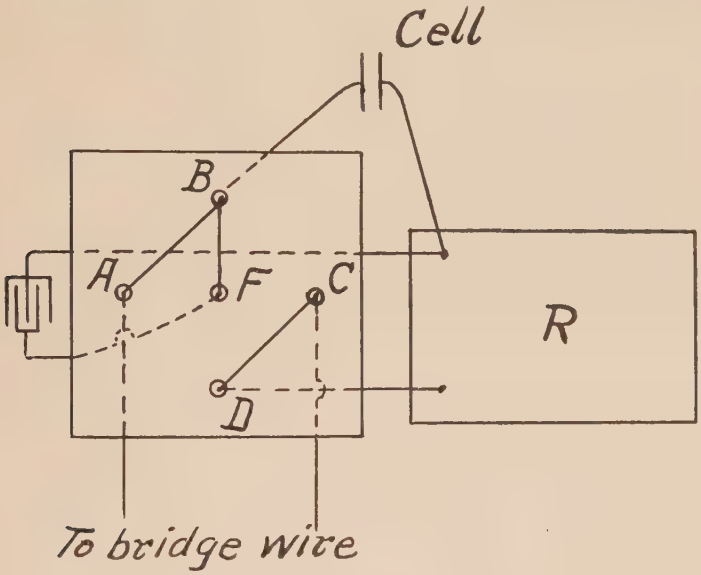

Fig. 2.

The Commutator.—In order to eliminate contact resistances in all bridge connections, a commutator is used, by means of which the cell and the comparison resistance R may be interchanged. If readings are taken in both positions these errors may be entirely eliminated as well as any error in the sliding contact. If a_1 and a_2 are the readings of the bridge in positions (1) and (2), respectively and r the length of the bridge wire we get

$$X = R \frac{r + (a_1 - a_2)}{r - (a_1 - a_2)}$$

where as before X is the electrolytic and R the comparison resistance.

The commutator is shown in Fig. 2. It consists of the mercury cups A, B, C and D in a block of paraffin about six inches square and three inches deep. The connection of A to B and C to D gives position (1)

while A to D and B to C gives position (2). The additional mercury cup F is connected to the condenser and permits a quick change of the position of that instrument. When F is joined to B it is in parallel with the cell and when joined to D it is in parallel with the resistance R.

The Test Experiments.

In order to obtain definit figures illustrating the degree of precision attainable with the new apparatus, a series of test experiments were carried out, in which solutions of various concentrations were measured in different forms of cells. The cells employed in most of these experiments will be referred to as Nos. 1, 2, 3, and 4, respectively. They were of the pipet type described by MacInnes.[1] The first three cells had platinized electrodes, 10 mm. in diameter and 75 mm., 15 mm., and 2 mm. apart, respectively. Cell 4 was fitted with two circular, unplatinized, platinum electrodes 30 mm. in diameter and 1.5 mm. apart. During the measurements the cells were submerged in a water thermostat maintained at room temperature to within 0.003° during the measurement of any cell.

The "extended" bridge wire was used in all the experiments and the high-frequency machine was driven at its normal rate, giving a frequency of 1000 cycles per second. Except where otherwise specified, the resistance boxes employed were standard, high-grade boxes with manganin resistance coils. The special "film" resistance box described above was employed only in the measurement of very high resistances.

In order to eliminate the personal element as far as possible most of the measurements were made in triplicate, that is, the bridge setting for each cell was determined *independently* by three different observers.[2] In recording the results thus obtained, the value for the resistance of the cell (in ohms) obtained by each observer is given, together with a statement of the number of scale divisions through which it was necessary to swing the contact in deciding the proper setting. A "*perfect minimum*" means that *perfect silence* was obtained at one point and that a sound was heard if the contact was moved more than 0.1 scale division on either side of this point. In this connection it may be noted that the tones obtained on the two sides of the minimum were identical in all their properties and were perfectly clear and of uniform quality.

As a basis for comparison of the degrees of precision attained in the different experiments the mean of the three results is given, together with the maximum and the average deviations from this mean, expressed in per cent.

Experiment 1.—The electrolyte was 0.1 *N* KCl and its resistance in cell No. 1 was determined. The results in ohms obtained by the three

[1] Dissertation, 1911; *J. Am. Chem. Soc.*, **33**, 1688 (1911).

[2] I wish to acknowledge my obligations to Mr. G. Y. Williams for his efficient assistance in carrying out this series of test experiments.

observers are as follows: 248.177, 248.172, 248.182; mean, 248.177; max. d., 0.002%; a. d., 0.0014%. Perfect minimum.

Experiment 2.—0.01 *N* KCl in cell 2. Resistance, 414.854, 414.862, 414.867; mean, 414.861; max. d., 0.0017%; a. d., 0.0012%. Perfect minimum.

Experiment 3.—0.001 *N* KCl in cell 2. Resistance, 4007.60, 4007.60, 4007.76; mean, 4007.65; max. d., 0.0027%; a. d., 0.0017%. Perfect minimum.

Experiment 4.—0.001 *N* KCl in cell 3. Resistance, 541.779, 541.774, 541.794; mean, 541.782; max. d., 0.0018%; a. d., 0.0015%. Perfect minimum. Owing to the small heat capacity of the thin film of liquid between the electrodes in this cell, the heating effect of the current made it necessary to make the final bridge setting very quickly. The time consumed in this operation varied from 6.4 sec. to 8.0 sec. with the different observers.

Experiment 5.—0.0001 KCl solution in cell 2. Resistance, 30,892, 30,894; mean, 30,893; dev., 0.003%. Minimum extended through 3 scale divisions.

Experiment 6.—Identical with Experiment 5 except that the special "film" resistance box was substituted in place of the Hartman and Braun box used in experiment 5. Resistance, 28,895.8, 28,896.3; mean, 28,896.0; dev., 0.0011%. Perfect minimum. A comparison of the results of Experiments 5 and 6 shows the improvement in the minimum. effected by use of the film resistances.[1]

Experiment 7.—Conductivity water having a specific conductance of $0.9.10^{-6}$ mhos at the temperature of the experiment was measured in cell 4. Resistance, 33,185, 33,191; mean, 33,188; dev., 0.012%. Poor minimum. No point of complete silence could be found. A swing of 12 scale divisions was necessary in estimating the bridge setting.

Experiment 8.—The same as Experiment 7 except that the special "film" resistance box was employed. Resistance, 32,857.9, 32,857.9, 32,857.9; mean, 32,857.9; dev., 0.0%. Minimum good, perfect silence being obtained. Range of swing 4 scale divisions, with sharp appearance of the sound at each end of the swing. The advantage of the "film" resistances is again evident from the results of Experiments 7 and 8. The next three experiments deal with solutions of high specific conductance.

Experiment 9.—Normal KBr in cell 1. Resistance, 27.9293, 27.9296, 27.9296; mean, 27.9295; max. d., 0.0007%; a. d., 0.0005%. Perfect minimum. This experiment shows that polarization has no influence upon the minimum at this concentration.

[1] The difference in the absolute values of the resistances given in Experiments 5 and 6 is not significant, as the values used for the resistance units of the "film" resistance box are only approximate. No attempt was made to standardize these resistances for this set of experiments.

Experiment 10.—6 *N* H_2SO_4 in an Arrhenius cell with the electrodes 10.2 cm. apart. Resistance, 1.5506, 1.5512, 1.5518; mean, 1.5512; max. d., 0.04%; a. d., 0.028%. Minimum very poor. Length of swing 40 scale divisions. The disturbing effect of polarization is evident in this experiment. It can be largely eliminated, however, by employing a properly designed cell, as is evident from the results of the next experiment.

Experiment 11.—6 *N* H_2SO_4 in a special high resistance cell (Kohlrausch and Holborn, Fig. 10, p. 16) fitted with platinized electrodes 3 cm. in diameter. Resistance, 149.401, 149.407, 149.425, 149.407; mean, 149.410; max. d., 0.010%; a. d., 0.005%. Minimum fair. Range of swing, 1 scale division. Complete silence was not obtained.

Experiment 12.—In measuring the resistance of very dilute solutions, fair results can also be obtained with a small induction coil, provided that "film" resistances are employed instead of the standard type of resistance box. The following results were obtained in this manner for a 0.0001 *N* KCl solution in cell 2: Resistance, 28,927.6, 28,928.9; mean, 28,928.2; dev., 0.003%. Minimum good. Perfect silence was obtained. Range of swing 3, scale divisions (cf. Exp. 6).

When the standard resistance box was used the following results were obtained: Resistance, 30,096, 30,102; mean, 30,099; dev., 0.01%. Minimum very poor. Silence could not be secured at any point. Range of swing, 20 scale divisions (cf. Exp. 5).

Discussion of the Experiments.

The results obtained in the test experiments indicate very clearly that with the improved apparatus *the conductivity of any solution of an electrolyte from conductivity water itself up to a several-times-normal solution can be determined with a precision of 0.01% with the greatest of ease, and that by careful work this degree of precision can be raised to 0.001% in most cases.*

Although a *precision* of a few thousandths of 1% can be obtained with this apparatus, the attainment of an equal degree of *accuracy* is of course quite another story, involving as it does the elimination of all sources of constant error, amounting to 0.001% or more.

In cases where *changes* in conductance, *only*, are involved, however, constant sources of error are not necessarily objectionable. An example of this occurs in transference measurements by the Hittorf method. At the completion of such a transference experiment it is first necessary to discover whether the concentration of the three middle portions are identical or not. This can be very quickly and accurately determined by finding successively the bridge settings for each solution in the same conductance cell. This method will usually result in the saving of a considerable amount of time, since in exact work these concentrations must be determined with an accuracy of at least 0.01%. The new apparatus should prove of considerable value in all cases where a very exact analytical control of pure solutions of electrolytes is desired.

PART III.—PREPARATION AND PRESERVATION OF SOLUTIONS.

Preparation of Pure Water.—Attention has already been called to the necessity of having water of low conductivity for the preparation of solutions. It has also been pointed out that the best water hitherto used for conductance work was that made by Kohlrausch and Maltby[1] with a specific conductivity of 0.9×10^{-6} mhos at 18° C. which involved a water correction of about 9% when used for preparing 0.0001 normal solutions of NaCl. Now, it is a comparatively easy matter to get water much purer than this from a good still made of copper and lined throughout with block tin. A still of this description having a capacity of about 50 liters is in use in this laboratory. By carrying out the distillation in air, water has been obtained which as a specific conductance five times smaller than the water used by Kohlrausch and Maltby.

In order to get the best water the still is filled with the ordinary distilled water of the laboratory to which are added 150 cc. of an alkaline permanganate solution containing 8 g. $KMnO_4$ to 200 g. KOH in a liter of solution. The contents of the still are then heated by a steam heating coil until water begins to come over, when the steam is turned off. It is allowed to stand over night and the distillation carried out the next day. The first part of the distillate—eight to ten liters—will contain practically all of the ammonia and is rejected; good water can now be collected. The end of the block-tin condenser tube is extended into the mouth of the collecting bottle and the water collected in an atmosphere of steam. For the best results it is necessary to have the steam only partially condensed to liquid water and, consequently a vigorous current of steam issuing from the mouth of the bottle. The water thus collected is boiling hot. If these precautions are observed, it is a simple matter to get water which has a specific conductance of 0.25×10^{-6} reciprocal ohms at 25° C. Water of this purity has repeatedly been obtained by both Mr. Williams and myself. By taking special precautions, such as, repeatedly rinsing the collecting bottle with the boiling hot distillate, collecting in an especially vigorous current of steam and taking the distillate after the still was half emptied, water has been found with a specific conductance of 0.19×10^{-6} reciprocal ohms at 25° C. This sample for the water conductivity cell was taken from the bottle filled up nearly to the top of the ground glass part and while the distillation was still going on. The conductivity arose, on standing sixteen hours in the collecting bottle, to 0.27×10^{-6}.

A scheme was devised for subjecting this distillate to a second distillation adding to the still some phosphoric acid instead of the permanganate solution. In this way water having a conductivity of 0.17×10^{-6} mhos was obtained.[2]

[1] *Loc. cit.*

[2] Mr. E. B. Millard has since obtained water measuring 0.15×10^{-6} mhos, without the use of the second still.

Preservation of Water.—Exposure of very pure water to contact with ordinary air, if only for a few minutes, suffices to materially increase the conductivity. Protecting it from the atmosphere, however, shows that the conductivity is much more constant. This constancy depends on the efficiency of the protection. If ground glass stoppers are used they may furnish ample protection after they are inserted, but in putting them in place or removing them small particles of impurities that have collected about the mouth of the vessel may be loosened and fall in. Furthermore, by turning the stopper and rubbing together the ground surfaces, very small particles of glass may be found which have a greater polluting power than other glass. (It seems probable that water in contact with ground glass surfaces is more easily contaminated than if in contact with glazed surfaces only.)

A better means of protection is to cover the bottle (or flask) with a watch glass and invert over it a beaker, just large enough to slip over the neck of the bottle. A still better way is to cover with several layers of tin foil, pressing it down around the mouth of the bottle to make the passage of air difficult. The tinfoil should be thoroughly steamed before using. Both of these schemes employ the better plan of having a covering fit *over* the mouth of the bottle rather than something to fit *into* it. Using tin foil, Williams, who suggested it, kept water for a day before its conductivity rose to 0.36×10^{-6} and for several weeks before it rose to 0.6×10^{-6}. Recently, I have kept some of the best water yet obtained for sixteen hours in a resistance glass bottle with the conductivity rising from 0.19×10^{-6} to 0.27×10^{-6} at 25° C. This water was boiled hot at the beginning and was in contact with ground glass until on cooling, contraction brought it down out of the ground glass mouth of the bottle.

The only perfect way of preventing contamination by the air is to distill *in vacuo* and collect in an air-tight vessel. If this vessel is made of the best glass, such as Jena-geräte or resistance glass the contamination will be very little indeed. In this case as in all others it is essential to wash and steam the vessel repeatedly in order to remove all traces of dirt or soluble parts of the glass. After many trials I was able to keep water that measured 0.21×10^{-6} mhos at 0° for twelve hours without any appreciable change in its conductivity. This is ample time for making up solutions and measuring their conductance. With water of this purity if the work is done *in vacuo*, reliable results should be obtained from 0.0001 N solutions, and from 0.00001 N solutions they should be as reliable as the present figures on 0.0001 N solutions.

The present work was undertaken at the suggestion of Professor E. W. Washburn, and has been carried out under his direction. Professor Washburn has always been ready with fruitful suggestion and methods of attack, and my thanks are due him for his assistance and encouragement.

VITA.

The writer received his early education in the public schools of Ohio and his college preparatory work in the school now known as Ohio Northern University. In 1903 he went to the University of Chicago where, after two and a half years' work, he received the B.S. degree in 1905. During the years 1905–'08 he was teacher of chemistry and physics in Ottawa, Illinois, Township High School. In 1908 he returned to the University of Chicago for two years of graduate work and in 1910 went to the University of Washington for one year as instructor in chemistry. From 1911 to 1913 he has done graduate work and teaching in the department of chemistry of the University of Illinois.